Terminal Electron Acceptor Mass Balance: Light Nonaqueous Phase Liquids and Natural Attenuation

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Abstract: Light nonaqueous phase liquids (LNAPLs) in subsurface systems may contain a relatively large amount of biodegradable organic material. During the biochemical oxidation of the organic compounds in the LNAPL, electrons are transferred to terminal electron acceptors (TEA) [i.e., O_2, NO_3^-, Mn(IV), Fe(III), SO_4^{-2}, CO_2] via coupled redox reactions. A mass balance between the TEA required for mineralization of benzene, toluene, ethyl benzene, and xylene (BTEX) compounds contained in the subsurface (ground water, soil, LNAPL) and the total TEA available from the ground water and aquifer sediments is proposed and evaluated. The total TEA available is predominantly attributed to the solid phase material; the aqueous phase TEA constitutes a minor amount; and the TEA required for BTEX mineralization is predominantly from the LNAPL. Consequently, a TEA deficit exists in the LNAPL source area. Under these conditions, it may be invalid to assume an infinite supply of TEA and sustained bioattenuation rates. LNAPL removal is one remedial option to reduce the TEA deficit in the source area.

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Introduction

Background

Sites contaminated with light nonaqueous phase liquids (LNAPLs) are often considered for a monitored natural attenuation (MNA) remedy. A critical analysis of natural attenuation often includes determining (1) whether the ground water plume is expanding, decreasing, or at steady state, and (2) the current and future assimilative capacity of the aquifer. Diagnostic tools currently used to make such determinations generally do not adequately consider LNAPL sources, heterogeneous sources of terminal electron acceptor (TEA), or the finite nature of TEA in the aquifer. Further, it is sometimes assumed that current rates of bioattenuation are sustained many years into the future and the rates continue even when sources of TEA are depleted. This assumption may be invalid if the solid and aqueous phase TEA in a source area is significantly diminished or depleted altogether. The potential for this condition exists at sites containing LNAPLs. The long term sustainability of bioattenuation rates requires further study to ensure MNA is protective of public health and the environment (Bekins et al. 2001).

A mass balance is proposed and evaluated where the TEA required for mineralization of BTEX found in the LNAPL, solid, and aqueous phases is compared to the bioavailable TEA found in the aquifer sediments and ground water. Such a comparison can be used to help assess the assimilative capacity of an aquifer and critically evaluate assumptions used in the feasibility analysis of natural attenuation.

Bioattenuation

Micro-organisms obtain energy and carbon for new cell material through biochemical redox reactions in which electrons are transferred from organic contaminants to TEA. Biochemical redox reactions will be limited in systems without TEA.

Under aerobic conditions, oxygen is the most energetically favorable TEA. However, due to the low solubility of oxygen, dissolved oxygen (DO) is rapidly depleted in ground water. Subsequently, anaerobic conditions may result where the biochemical oxidation of organic compounds also occurs (Lovley and Phillips 1986; Suflita et al. 1988; Hutchins et al. 1998). The sequential order of TEA utilization under anaerobic conditions is nitrate (NO_3^-), manganese [Mn(IV)], ferric iron [Fe(III)], sulfate (SO_4^{-2}), and carbon dioxide (CO_2). Although biodegradation of BTEX has been correlated with this sequential utilization of TEA under field conditions (Borden et al. 1995), the distribution of the terminal electron accepting processes is highly dynamic in both time and space (Vroblesky and Chapelle 1994).

The TEAs O_2, NO_3^-, SO_4^{-2}, and CO_2 are generally found in the aqueous phase. However, in sulfate-rich environments, SO_4^{-2} may also be derived from aquifer sediments. Ferric iron is found in abundance and is present in the solid phase since it is slightly soluble in the near neutral pH range. Ferrous iron [Fe(II)] is the byproduct of Fe(III) reduction and is used as a general indicator of anaerobic biodegradation. Accurate measurement of CO_2 pro-

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duced during biodegradation is difficult because carbonate in ground water (measured as alkalinity) serves as both a source and sink for free CO_2 (Rifai et al. 1998). Consequently, measurement of the reaction byproduct, methane (CH_4), is used as a quantitative indicator of the role of CO_2.

Bioavailability and Measurement of Solid Phase TEA

Fe and Mn species and reducible organic matter are the primary sources of solid phase TEA in aquifers (Heron et al. 1994a). However, their bioavailability is not straightforward and only a fraction of their total amount measured in subsurface systems is bioavailable and reducible under field conditions. Currently, the reducibility of aquifer organic matter is poorly understood and unquantifiable, and manganese species typically contribute 2–5% of the total transferrable electron equivalents (Heron et al. 1994a). For these reasons, only solid phase TEA composed of Fe was considered in this analysis.

Soil samples collected from five sites indicated 5–10% of the total Fe was bioavailable (Evans et al. 1999). Natural and man-made amorphic iron oxides are readily reduced (microbially) (Lovley and Phillips 1988) whereas more crystalline forms [goethite (α-FeOOH), akaganeite (β-FeOOH), hematite (α-Fe_2O_3), magnetite (Fe_3O_4)] are poorly reduced even with extended incubation (Lovley and Phillips 1986, 1987, 1988). Some microbial reduction of synthetic crystalline Fe(III) oxides has been reported and a correlation of the long term reduction with oxide surface area was observed (Roden and Zachara 1996). Increasing order of crystallinity corresponds to a decreasing order of Fe(III) bioavailability [i.e., ferrihydrite rust ($Fe(OH)_3$), lepidocrocite (γ-FeOOH), akageneite, goethite, and hematite] (Kennedy et al. 1999).

Fe(II) produced from Fe(III) reduction may limit Fe(III) oxide reduction by sorption and saturation of the Fe(III) surface due to the high stability of the Fe(III)–O–Fe(II) interaction (Roden and Zachara 1996). Amorphous Fe(III) oxyhydroxide was bioavailable and readily reduced, but Fe_3O_4 and the mixed Fe(III)–Fe(II) compounds produced as a result of the reduction of amorphous Fe(III) oxyhydroxide were extractable but not reducible (Lovley and Phillips 1986). Ultimately, precipitation of Fe(II) may influence the bioavailability of Fe(III). If Fe(II) precipitates, this will likely cause the gradual "fouling" of the Fe(III) surface, steadily reducing the rate of iron reduction and should be considered in any long-term evaluation of intrinsic bioremediation (Howard and Kao 1997).

A brief overview of specific TEA bioavailability measurement methods and the corresponding values is presented and summarized in Table 1. Extensive reviews of these methods can be found elsewhere (Heron et al. 1994b; Christensen et al. 2000). A good correlation was established between the hydroxylamine-extracted Fe(III) and microbial reduction of Fe(III) (Lovley and Phillips 1987a). Modifications of this general method involving HCl extraction have been subsequently used to quantify bioavailable Fe(III). Some minerals are HCl resistant (0.5 M) including pyrite, marcasite, goethite, lepidocrocite, and hematite. HCl-extractable minerals include ferric gel, protoferrihydrite, ferrihydrite, maghematite (γ-Fe_2O_3), some iron in clay, ferrous carbonate, ferrous phosphate, green rusts, magnetite, acid-volatilized sulfides, mackinawite, amorphous FeS, and greigite (Fe_3S_4) (Lyon et al. 1997).

A weak HCl extraction (0.5 M, 24 h) method dissolved a specific mineral fraction by attacking ion-exchangeable Fe(II), ferrous monosulfides, amorphous Fe(III) oxides and ferrihydrite, part of siderite and akageneite, and a small fraction of iron oxides (Heron et al. 1994b). HCl extraction (0.5 M, 48 h) of Fe(III) from contaminated aquifer sediments indicated inverse Fe(III) and Fe(II) concentrations suggesting the role of Fe(III) in the bioattenuation process (Kennedy et al. 1999). In uncontaminated areas, Fe(III) concentrations were measured greater than 3.6 mmol/kg. At another site, HCl extraction (0.5 M, 1 h) of bioavailable Fe(III) values ranged from 0.09 to 2.6 mmol/kg ($n=22$) (Lendvay et al. 1998). Samples ($n=4$) in which dissolved oxygen was present in significant quantities (0.06–0.25 mM DO) were highest in Fe(III) and used to estimate bioavailable Fe(III). Samples collected from three cores in aerobic, uncontaminated aquifer material and extracted (0.5 M, 24 h) contained Fe(III) ranging from 1.2 to 6.9 mmol/kg (Lyon et al. 1997). Similar extraction procedures (0.5 M, 24 h) at another site yielded an average value of 5.9 mmol/kg Fe(III) (Howard and Kao 1997). Some contamination may have been present and values may not represent background Fe(III). The average total Fe [Fe(II)+Fe(III)] was 6.4 mmol/kg. The total extractable iron using a 6 M HCl extraction procedure was 20.7 mmol/kg ($n=12$), suggesting that approximately 70% of the total iron was not bioavailable.

A direct method involving Fe-reducing bacteria was developed to quantify bioavailable Fe (Evans et al. 2000). The method involved a slurry of the aquifer sediment, an electron donor, lyophilized *Shewanella alga* BrY, mineral salts, and other reagents. After one month of incubation, the Fe was extracted with 1 mL concentrated HCl and analyzed. Results from one site indicated that the average bioavailable Fe(III) was 18.1 and 20.9 mmol/kg in samples collected at two locations (7.6–14.2 m bgs).

Bioavailable TEA measured in aquifer material is site specific (Table 1) and dependent on soil mineralogy. The most accurate estimate of bioavailable iron would require site specific, spatially representative aquifer samples analyzed via an appropriate method. However, correlations between laboratory methods and microbially reduced TEA have been established for several methods (hydroxylamine, mild acid extraction, direct Fe-reducing bacteria) suggesting reasonable approximations can be made. Too few sample analyses have been reported to establish an accurate correlation between aquifer mineralogy and TEA concentrations. Nevertheless, rough estimates of the bioavailable iron in aquifer material can be used to conduct a mass balance.

Light Nonaqueous Phase Liquids

LNAPLs are organic liquids that exist as a separate, immiscible liquid phase when in contact with water, have a density less than water, and are commonly comprised of petroleum fuel. Volumetric LNAPL saturation values compiled from several sites range from 10 to 20% and 15 to 50% in the unsaturated and saturated zones, respectively (Cohen and Mercer 1993). In a LNAPL source area, the range of volumetric LNAPL saturation can be as high as 70–90% (Weaver et al. 1994). Complexities associated with the relationship between the LNAPL thickness in a monitoring well and the actual LNAPL thickness in the aquifer (Marinelli and Durnford 1996) generally yields only rough approximations (Newell et al. 1995) of LNAPL saturation.

Petroleum fuel products are multicomponent organic mixtures, each with varying solubility. Compounds in fuel LNAPLs of significant regulatory interest include BTEX. Several factors affect their mass transfer from the LNAPL phase to the aqueous phase including ground water velocity, contact time and area, attenuation mechanisms, LNAPL saturation, solubility, temperature, permeability, etc. At equilibrium, the effective solubility of compo-

Table 1. Summary of Literature-Reported Values for the Bioavailable TEA [Fe(III)] in Aquifer Media

TEA (mmol/kg)	Media	Method	Comments
0–0.4[a]	Sand and gravel aquifer with clay lens (Pensacola, FL)	Hydroxylamine	Background samples collected from clay lens contained Fe(II) but no reducible Fe(III).
11.8, 17.9, 48.7[b]	Sandy glaciofluvial aquifer, reddish-gray, medium-to-coarse-grained sand (Vejen, Denmark)	0.5 M HCl 24 h	Two aerobic samples and one nitrate-reducing sample (avg.=26.2; s.d.=19.8, $n=3$).
3.6[c]	Fine-grained, quartz sandstone, 1–6% hematite, siltstone, and shale lenses (Norman, OK)	0.5 M HCl 48 h	Range of background Fe(III) not reported.
1–2.6[d]	Fine-to-medium sand, some silt, formed by an eolian/lacustrine modification of clay deposits (St. Joseph, MI)	0.5 M HCl 1 h	22 samples analyzed; the range reported here (avg.=2.00; s.d.=0.72, $n=4$) represented uncontaminated samples with appreciable oxygen concentration.
1.2–6.9[e]	Fine-to-coarse-grained sand, some clay (Victorville, CA)	0.5 M HCl 24 h	Avg. Fe(III) concentration was 2.4 mmol/kg ($n=12$).
2.2–25.7[f]	Alluvial sand, silt, and clay; soil textures were sand, loamy sand, sandy loam (Cumberland Co., NC)	0.5 M HCl 24 h	Avg. Fe(III) was 5.9 mmol/kg ($n=12$); total Fe(II)+Fe(III)=6.4 mmol/kg
18.1,20.9[g]	Sand, silty sand (Sacramento, CA)	Fe-reducing bacteria+lactate	Averages for two separate cores ($n=4$ each); greater bioavailable Fe(III) was measured in the silty sand zone than in the sand zone.

Note: An arbitrary range of solid phase TEA values was established; low <4, medium 4–12, and high 12–49 mmol/kg. Solid phase bioavailable Fe concentrations of 2, 8, and 31 mmol/kg were selected as representative of low, medium, and high values.

[a]Lovley and Phillips (1987).

[b]Heron et al. (1994b).

[c]Kennedy et al. (1999).

[d]Lendvay et al. (1998).

[e]Lyon et al. (1997).

[f]Howard and Kao (1997).

[g]Evans et al. (1999).

nent i (S_i^e) [Eq. (1)] in water is based on the solubility of the pure phase compound in water (S_i), and the mole fraction of the component i in the LNAPL mixture (X_i) (Feenstra et al. 1991).

$$S_i^e = X_i S_i \tag{1}$$

The water solubility (S_i) of BTEX (20 °C) is 1780, 515, 152, and 189 mg/L for benzene, toluene, ethyl benzene, and total xylenes, respectively (U.S. EPA 1990).

Theoretical Development

The total TEA required (TEA_R) (mol e^-) for complete BTEX mineralization is estimated based on the mass of BTEX present in the LNAPL, solid, and aqueous phases, and the biodegradation stoichiometry. The total TEA available (TEA_T) (mol e^-) in the subsurface is derived from both the aqueous and solid phase sources. Values of TEA_T and TEA_R can be compared as a general indicator of whether sufficient TEA exists in the source area for mineralization of the BTEX. Balanced half reactions for complete mineralization indicate that the number of e^- equivalents required for complete mineralization per mole of BTEX (TEA_{BTEX}) is 30, 36, 42, and 42 mol e^-/mol, respectively (rxns 1–4).

Compound	Half reaction	Mol e^-/mol BTEX	
Benzene	$C_6H_6+12H_2O \rightarrow 6CO_2+30H^++30e^-$	30	(rxn 1)
Toluene	$C_7H_8+14H_2O \rightarrow 7CO_2+36H^++36e^-$	36	(rxn 2)
Ethyl benzene	$C_8H_{10}+16H_2O \rightarrow 8CO_2+42H^++42e^-$	42	(rxn 3)
Xylenes	$C_8H_{10}+16H_2O \rightarrow 8CO_2+42H^++42e^-$	42	(rxn 4)

Similarly, balanced half reactions can be used to estimate the number of e^- equivalents per mole of TEA utilized (NE_i) (rxns 5–10).

TEA	Half reaction	mol e^- TEA (NEi)	
O_2	$O_2+4H^++4e^- \rightarrow 2H_2O$	4	(rxn 5)
NO_3^-	$2NO_3^-+12H^++10e^- \rightarrow N_2+6H_2O$	5	(rxn 6)
Fe^{+3}	$FeOOH+HCO_3^-+e^- \rightarrow FeCO_3(s)+2H_2O$	1	(rxn 7)
Mn^{+4}	$MnO_2+HCO_3^-+3H^++2e^- \rightarrow MnCO_3(s)+2H_2O$	2	(rxn 8)
SO_4^{-2}	$SO_4^{-2}+9H^++8e^- \rightarrow HS^-+4H_2O$	8	(rxn 9)
CO_2	$CO_2+8H^++8e^- \rightarrow CH_4+2H_2O$	8	(rxn 10)

CH_4 was used to estimate the amount of CO_2 utilized as TEA;

1 mole CO_2 utilized/mole CH_4 measured was assumed. TEA_R for complete mineralization of contaminants in a representative 1 cubic meter (1 m^3) unit volume was estimated based on the total mass of BTEX contained in the water phase ($TEA_{R\text{-}AQ}$), adsorbed to the solid phase ($TEA_{R\text{-}S}$), and contained in the LNAPL phase ($TEA_{R\text{-}LNAPL}$) [Eq. (2)].

$$TEA_R = TEA_{R\text{-}AQ} + TEA_{R\text{-}S} + TEA_{R\text{-}LNAPL} \quad (2)$$

$TEA_{R\text{-}AQ}$ (mol e^-) is estimated assuming equilibrium between the LNAPL and aqueous phases.

$$TEA_{R\text{-}AQ} = \Sigma_{BTEX} V_T \eta (1 - \theta_{LNAPL}) X_i S_i TEA_{BTEX} / MW_{BTEX} \quad (3)$$

$TEA_{R\text{-}S}$ (mol e^-) is estimated assuming equilibrium between the solid and aqueous phases.

$$TEA_{R\text{-}S} = \Sigma_{BTEX} V_T f_{OC} k_{OC} X_i S_i \rho_B TEA_{BTEX} / MW_{BTEX} \quad (4)$$

$TEA_{R\text{-}LNAPL}$ (mol e^-) is estimated based on the mass fractions of BTEX in the LNAPL.

$$TEA_{R\text{-}LNAPL} = \Sigma_{BTEX} V_T \eta \theta_{LNAPL} \rho_{LNAPL} f_{BTEX} TEA_{BTEX} / MW_{BTEX} \quad (5)$$

where

TEA_R = total TEA required for complete mineralization of BTEX (mol e^-);
$TEA_{R\text{-}AQ}$ = fraction of TEA_R attributed to BTEX in the aqueous phase (mol e^-);
$TEA_{R\text{-}S}$ = fraction of TEA_R attributed to BTEX in the solid phase (mol e^-);
$TEA_{R\text{-}LNAPL}$ = fraction of TEA_R attributed to BTEX in the LNAPL (mol e^-);
Σ_{BTEX} = sum of BTEX components;
V_T = unit volume of aquifer (1 m^3);
η = porosity (cm^3 pores/cm^3 solid);
θ_{LNAPL} = volumetric LNAPL saturation (cm^3 LNAPL/cm^3 pore);
X_i = mole fraction of BTEX component i in the fuel mixture (mol/mol);
S_i = pure phase solubility of BTEX component i in water (mg/L);
TEA_{BTEX} = moles e^-/moles of BTEX component i mineralized (mol/mol);
MW_{BTEX} = molecular weight of BTEX component i (g/mol);
f_{OC} = fraction of organic carbon in aquifer (mg OC/mg aquifer material);
k_{OC} = organic carbon water partition coefficient (L/kg OC);
ρ_B = bulk density (g/cm^3);
ρ_{LNAPL} = density of LNAPL (g LNAPL/cm^3 LNAPL); and
f_{BTEX} = mass fraction of BTEX component i in LNAPL (g BTEX/g LNAPL).

Total TEA available (TEA_T) is calculated based on the site specific content of the aquifer system in both the aqueous ($TEA_{T\text{-}AQ}$) and solid ($TEA_{T\text{-}S}$) phases.

$$TEA_T = TEA_{T\text{-}AQ} + TEA_{T\text{-}S} \quad (6)$$

$$TEA_{T\text{-}AQ} = \Sigma_{TEA} (V_T \eta (1 - \theta_{LNAPL}) [TEA]_i NE_i / MW_i) \quad (7)$$

$$TEA_{T\text{-}S} = \Sigma_{TEA} (V_T \rho_B [TEA]_i NE_i / MW_i) \quad (8)$$

where

TEA_T = total TEA available in the subsurface for biochemical reaction (mol e^-);
$TEA_{T\text{-}AQ}$ = fraction of TEA_T available in the aqueous phase (mol e^-);
$TEA_{T\text{-}S}$ = fraction of TEA_T available in the solid phase (mol e^-);
Σ_{TEA} = sum of each TEA constituent used during BTEX mineralization;
$[TEA]_i$ = concentration of TEA constituent i [$TEA_{T\text{-}AQ}$(mg/L), $TEA_{T\text{-}S}$ (mmol/kg)];
NE_i = number of e^- transferred/mole TEA (mol e^-/mol TEA); and
MW_i = molecular weight of TEA constituent i (g/mol).

A critical analysis of the TEA mass balance is accomplished with the use of two parameters to balance the deficit between TEA_R and TEA_T: aqueous phase pore volume (PV) and equivalent solid phase volume (ESV). These parameters serve as general indicators to evaluate TEA abundance and are not intended to serve as quantitative indicators to predict the extent of plume propagation.

$$PV = (TEA_R - TEA_T)/(TEA_{T\text{-}AQ}) \quad (9)$$

$$ESV = (TEA_R - TEA_T)/TEA_T \quad (10)$$

PV provides a conceptual estimate of the volume of ground water containing $TEA_{T\text{-}AQ}$ that must be transported into the representative volume (source area) to balance the TEA deficit. ESV provides a conceptual estimate of the additional aquifer volume, including both the aqueous and solid phases, required to balance the TEA deficit.

BTEX compounds generally represent a large fraction of water soluble compounds derived from petroleum fuels. Based on the effective solubility, an analysis of four fuels, fresh gasoline, two weathered gasolines, and fresh JP-4 indicated that BTEX compounds comprised 68, 89, 68, and 95% of the soluble compounds, respectively (Rifai et al. 1998). Numerous non-BTEX compounds found in fuel mixtures include alkanes, cycloalkanes, branched alkanes, and naphthalenes (Johnson et al. 1990; U.S. DHHS 1993) and are also biodegradable. Biodegradation of these compounds will occur in subsurface systems representing a sink for TEA which subsequently will not be available for biodegradation of BTEX compounds. An adjustment for this TEA sink in biodegradation modeling can be accomplished by reducing the TEA/biodegradation-byproduct concentrations by a factor such as the ratios of BTEX/TOC or BTEX/BOD or simply by 30% (Rifai et al. 1998). In the analysis presented here, only BTEX compounds were considered.

Results

Mass Balance Calculations for an Unnamed Site

A large volume of jet fuel (JP-4) LNAPL was released at the site. BTEX analysis of separate LNAPL samples collected from nine wells on three sampling events indicated the following average mass fractions of BTEX; benzene 0.0051 (s.d. 0.0027, $n = 11$), toluene 0.02 (s.d. 0.0085, $n = 11$), ethyl benzene 0.012 (s.d. 0.0062, $n = 11$), and xylenes 0.022 (s.d. 0.0055, $n = 11$) (Table 2). Mass fractions were converted to mole fraction based on the average molecular weight (127.6 g/mol) of JP-4 determined from chemical analyses of the LNAPL. Monitoring well LNAPL thickness routinely ranged between 2 and 20 ft (0.6–6.1 m) in differ-

Table 2. BTEX Mass Fraction and TEA Parameter Values to Estimate (1) the TEA Required ($TEA_{R\text{-}LNAPL}$, $TEA_{R\text{-}S}$, $TEA_{R\text{-}AQ}$,) for Complete Mineralization of BTEX Compounds in JP-4 Fuel and (2) the total TEA Available (TEA_T) in the Aquifer Matrix (i.e., Aqueous and Solid Phases)

			TEA required for complete BTEX mineralization[b]		
	JP-4 BTEX[a]		LNAPL	Solid	Ground water
	Mass Fraction	Mole Fraction	($TEA_{R\text{-}LNAPL}$)	($TEA_{R\text{-}S}$)[c]	($TEA_{R\text{-}AQ}$)
Contaminant	(f_{BTEX})		(mol)	(mol)	(mol)
Benzene	0.0051	0.0084	99.2	2.0	1.7
Toluene	0.02	0.027	386.8	7.4	1.6
Ethyl benzene	0.012	0.014	239.9	3.1	0.25
Xylene	0.022	0.027	443.2	7.3	0.58
Total	0.0591	0.077	Subtotal 1169.2 (98%)	19.8 (1.7%)	4.1 (0.3%)
			Total (TEA_R) = 1193.1		

		TEA available (TEA_T) in unit volume of aquifer[b] (mol)
Electron Acceptor	Concentration	
Aqueous ($TEA_{T\text{-}AQ}$)		
DO (mg/L)	7[d]	0.25 (0.5)
NO_3^- (mg/L)	8.5	0.2 (0.4)
SO_4^{-2} (mg/L)	200	4.8 (8.8)
CO_2[e] (mg/L)	1.4	0.1 (0.1)
Solid ($TEA_{T\text{-}S}$)		
Fe(III) (mg/kg)	1700	49.6 (90.2)
	Total	54.9

Note: $V_T = 1\ m^3$, $\eta = 0.35$, $\rho_B = 1.6\ g/cm^3$, $\theta_{LNAPL} = 0.17\ cm^3$ LNAPL/cm^3 pore, $\rho_{LNAPL} = 0.85\ (g/cm^3)$.

[a]Average BTEX mass fraction = 0.059; average BTEX mole fraction = 0.077.

[b]Percent total in parenthesis.

[c]Sand-$f_{OC} = 0.0033$; clay and fine, medium, coarse silt-$f_{OC} = 0.02$–0.03 (Karickoff et al. 1979).

[d]Assumed value.

[e]CH_4 was measured in the subsurface at 0.5 mg/L and used to estimate CO_2 (see the text).

ent wells ($n = 7$) in the source area. Based on LNAPL thicknesses, physical characteristics of JP-4 and the aquifer material, calculations involving the NTHICK utility in a hydrocarbon spill screening model (Weaver et al. 1994) resulted in estimates of $\theta_{LNAPL} > 0.17$.

The representative volume of source area aquifer material used in the example calculation is 1 cubic meter (1 m^3). No site specific data were available for $TEA_{T\text{-}S}$ so 31 mmol/kg (1700 mg/kg) of bioavailable Fe(III) was assumed (refer to Table 1). SO_4^{-2} and NO_3^- concentrations in 7–8 uncontaminated wells were 200 mg/L ($n = 7$, three sampling events) and 8.5 mg/L ($n = 8$, three sampling events), respectively. A solubility analysis involving Ca^{+2} and SO_4^{-2} indicated that the solution was undersaturated (data not included). No solid phase contribution of sulfate, manganese, and organic matter TEA was assumed. Upgradient DO was assumed to be 7 mg/L. CH_4 was estimated to be 0.5 mg/L and was based on the average value of CH_4 in ten contaminated wells ($n = 10$, three sampling events). TEA_R and TEA_T were estimated using Eqs. (2)–(8). Site-specific and literature-reported parameter values are summarized in Table 2.

The majority of the TEA_R is due to the LNAPL (98%) with smaller fractions due to solid (1.7%) and aqueous (0.3%) phases. In sand material ($f_{OC} = 0.0033$), $TEA_{R\text{-}S} = 19.8$ moles, which comprises 1.7% of the total. The site also contains clay and silt material ($f_{OC} = 0.02$–0.03) yielding higher estimates of $TEA_{R\text{-}S}$ (120–180 mol, 9–13% of total). These results illustrate the relative small contribution of $TEA_{R\text{-}AQ}$ to TEA_R.

Solid phase TEA comprised the largest fraction (90.2%) of TEA_T. Due to the high concentration of SO_4^{-2} (200 mg/L), $TEA_{T\text{-}AQ}$ accounted for 9.8% of the TEA_T. Assuming a medium range value for bioavailable Fe [i.e., $TEA_{T\text{-}S} = 8$ mmol/kg (447 mg/kg), Table 1], the majority (69%) of the TEA_T is still attributed to solid phase TEA.

Approximately 21 times (ESV≈21) the TEA contained in the representative volume or 212 pore volumes (i.e., PV≈212) of influent $TEA_{T\text{-}AQ}$ would be required to balance the TEA deficit for BTEX mineralization. This suggests long term persistence of the source. PV and ESV would be greater at sites where higher values of θ_{LNAPL} and f_{BTEX} or lower values of TEA_T were representative. For example, assuming 8 mmol/kg $TEA_{T\text{-}S}$, $\theta_{LNAPL} = 0.25$, and $f_{BTEX} = 0.18$, the estimated ESV is 93 and PV>950. Given the site-specific parameter values (Table 2), the volumetric LNAPL saturation (θ_{LNAPL}) must be ≈0.005 for $TEA_R \approx TEA_T$.

Discussion

In this analysis, the total TEA required for mineralization of BTEX in the LNAPL source area is predominantly attributed to $TEA_{R\text{-}LNAPL}$ (98%), and $TEA_{R\text{-}AQ}$ represents a minor fraction (<0.3%). Solid phase TEA is a major source of TEA used in the biochemical reactions. However, it is the aqueous phase TEA and BTEX that are the focus of many natural attenuation feasibility studies. Studies that do not consider LNAPL and involve quantitative comparisons between upgradient $TEA_{T\text{-}AQ}$ and $TEA_{R\text{-}AQ}$ have limitations. For example, the $TEA_{T\text{-}S}$ contribution from iron is sometimes measured as the difference between upgradient and downgradient Fe(II) concentrations, and is assumed infinite. This

quantity is attributed to solid phase dissolution of Fe(III), which is finite, and given sufficient time can become depleted, especially in a LNAPL source area. Depletion of $TEA_{T\text{-}S}$ in the source area may significantly affect the fate and transport of BTEX. Fe(II) fouling of Fe(III) surfaces reduces Fe(II) concentrations in the aqueous phase and leads to lower lower levels of bioavailable Fe(III). These processes tend to interfere with an accurate assessment of the TEA contributed by Fe(III).

$TEA_{T\text{-}AQ}$ constituents decline and may become depleted during transport through the source area, yet mass transfer of BTEX from the LNAPL phase continually replenishes the aqueous phase concentrations of BTEX. Therefore, a simple comparison between upgradient $TEA_{T\text{-}AQ}$ and source area $TEA_{R\text{-}AQ}$ does not fully consider the dynamics of these processes. A quantitative analysis of the rates of contaminant transport and transformation, in conjunction with the effects of $TEA_{T\text{-}S}$ depletion and BTEX replenishment via LNAPLs, is needed to adequately assess rates and sustainability of natural attenuation under different sets of conditions. The significance of these effects must be determined on a site specific basis.

Contaminant transformation rates are routinely estimated from monitoring well data using a regression method based on a steady-state analytical model. Potential erroneous or even spurious transformation rates may arise because of the effects of dispersion, developing plumes, and too few data points which may lead to an overestimate of apparent transformation rates (McNab and Dooher 1998). Further, it may be inherently assumed in such analyses that the rate of reactions responsible for the existing BTEX plume also extends many years into the future. This assumption may be invalid for sites with large quantities of LNAPL in which the solid phase TEA is significantly diminished or depleted and the sequential utilization of TEA becomes less efficient with time. Quantification of $TEA_{T\text{-}S}$ and $TEA_{R\text{-}LNAPL}$ and their roles in natural attenuation will lead to an improved understanding of the long-term sustainability of transformation rates, and associated remedial timeframes.

In the example provided, oxygen reaeration of the ground water and volatile losses near the water table are assumed to be insignificant. The unsaturated zone (170 ft, 51.8 m) is multilayered with several low-permeability, high-moisture content zones that impede the reaeration flux. Additionally, soil in the unsaturated zone is highly contaminated (1000–25,000 mg/kg TPH) and biochemical reactions deplete the aqueous and gas phase TEA. Due to a slowly rising water table, the heavily contaminated saturated zone (20 ft, 6.1 m) is overlain by a heavily contaminated smear zone (25 ft, 7.6 m) with residual JP-4 extending nearly to the surface. Based on the extent of overlying contamination, BTEX loss from the representative volume was assumed negligible.

The diameter of the main LNAPL source area (assumed to be cylindrical) was estimated to be approximately 240–280 ft (73.2–85.4 m). The 0 mg/L total BTEX isopleth of the ground water plume was approximately 250 ft (76.2 m) from the edge of the LNAPL source area. Conceptually, the area constrained between the source area and the 0 mg/L isopleth is approximately equal to an equivalent source volume between 1 and 2. Using site-specific parameter values (Table 2), the ESV was estimated to be 21; i.e., 21 times greater TEA is required to balance the TEA deficit in the source area than is available in the source area. These results suggest that the BTEX plume will eventually expand beyond the current position. Such expansion is anticipated to be slow, however, due to $TEA_{T\text{-}S}$ available immediately downgradient and the high concentration of $TEA_{T\text{-}AQ}$ attributed to SO_4^{-2}.

LNAPL recovery techniques can be used to remove LNAPL and minimize the TEA deficit in source areas. For example, vacuum extraction, bioventing, skimming, and dual phase extraction have been used effectively for LNAPL recovery. Additionally, the use of surfactants, cosolvents, and thermal/steam injection are being developed under field conditions and are specifically designed to recover LNAPL. An alternative approach may be to inject an oxidant such as H_2O_2 to oxidize aquifer sediments for long term biochemical TEA utilization. Historically, H_2O_2 injection has been problematic for enhanced bioremediation due to rapid H_2O_2 decomposition, microbial toxicity, limited solubility of O_2, and loss of $O_2(g)$ to the unsaturated zone (Spain et al. 1989; Pardiek et al. 1992; Huling et al. 1991). Here, the primary purpose is not for immediate microbial use, but rather to provide a sustained long-term source of TEA_S. Oxidation of reduced aquifer sediments via H_2O_2 proceeds rapidly relative to microbially mediated decomposition (Barcelona and Holm 1991; Korom et al. 1996). Periodic oxidant injection into the subsurface may result in short term microbial inhibition but will increase the oxidation capacity of the aquifer material and shift the predominant terminal electron accepting process from an inefficient one (methanogenesis) to more efficient processes such as aerobic and/or iron and sulfate reduction.

Conclusions

A mass balance was performed between the TEA required for mineralization of BTEX contained in the LNAPL, solid, and aqueous phases found in a source area and the total TEA available from ground water and aquifer sediments. Results from a site specific example suggest that the total TEA available in the subsurface is predominantly attributed to the solid phase fraction; that the aqueous phase constitutes a minor fraction; and that the TEA required for BTEX mineralization is predominantly from the LNAPL with minor contributions from the aqueous and solid phases. Consequently a TEA deficit exists in the LNAPL source area. The large numbers of pore volumes (PV>200) of influent aqueous phase TEA or the equivalent solid volumes (ESV≈21) required to balance the TEA deficit suggests long term persistence of the source. In natural attenuation feasibility studies involving sites containing large amounts of LNAPL, it may be invalid to assume an infinite supply of solid phase TEA and sustained bioattenuation rates. LNAPL removal is one remedial option to reduce the TEA deficit in the source area.

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References

Barcelona, M. J., and Holm, T. R. (1991). "Oxidation-reduction capacities of aquifer solids." *Environ. Sci. Technol.*, 25(9), 1565–1572.

Bekins, B., Rittmann, B. E., and MacDonald, J. A. (2001). "Natural attenuation strategy for ground water cleanup focuses on cause and effect." *Eos Trans. Am. Geophys. Union,* 82(4), 53, 57–58.

Borden, R. C., Gomez, C. A., and Becker, M. T. (1995). "Geochemical indicators of intrinsic remediation." *Ground Water,* 33(2), 180–189.

Christensen, T. H., Bjerg, P. L., Banwart, S. A., Jakobsen, R., Heron, G., and Albrechtsen, H. J. (2000). "Characterization of redox conditions in groundwater contaminant plumes." *J. Contam. Hydrol.,* 45, 165–241.

Cohen, R. M., and Mercer, J. W. (1993). *DNAPL Site Evaluation.* CRC, Boca Raton, Fla, 314 pp.

Evans, P. J., Jones, K. A., Liu, C. C., and Lovley, D. R. (1999). "Development of a natural attenuation test kit. Natural attenuation of chlorinated solvents, petroleum hydrocarbons, and other organic compounds." *Proc. Fifth International In Situ and On Site Bioremediation Symposium,* Battelle, Columbus, Ohio, pp. 331–336.

Feenstra, S., Mackay, D. M., and Cherry, J. A. (1991). "A method for assessing residual NAPL based on organic chemical concentrations in soil samples." *Ground Water Monit. Rev.,* 11(2), 128–136.

Heron, G., Christensen, T. H., and Tjell, J. C. (1994a). "Oxidation capacity of aquifer sediments." *Environ. Sci. Technol.,* 28(1), 153–158.

Heron, G., Crouzet, C., Bourg, A. C. M., and Christensen, T. H. (1994b). "Speciation of Fe(II) and Fe(III) in contaminated aquifer sediments using chemical extraction techniques." *Environ. Sci. Technol.,* 28(9), 1698–1705.

Howard, K., and Kao, J. (1997). "Role of iron in the anaerobic biodegradation of fuel hydrocarbons." Rep. No. AL/EQ-TR-1997-0013 for the U.S. Air Force, Armstrong Laboratory, Tyndall Air Force Base, Fla.

Huling, S. G., Bledsoe, B., and White, M. (1991). "The feasibility of utilizing hydrogen peroxide as a source of oxygen in bioremediation." *Proc. International Symposium on In Situ Bioreclamation,* edited by R. E. Hinchee and R. F. Olfenbuttel, Batelle, Columbus, Ohio, pp. 83–102.

Hutchins, S. R., Miller, D. E., and Thomas, A. (1998). "Combined laboratory/field study on the use of nitrate for *in situ* bioremediation of a fuel-contaminated aquifer." *Environ. Sci. Technol.,* 32(12), 1832–1840.

Johnson, P. C., Stanley, C. C., Kemblowski, M. W., Byers, D. L., and Colthart, J. D. (1990). "A practical approach to the design, operation, and monitoring of *in situ* soil venting systems." *Ground Water Monit. Rev.,* 10(2), 159–178.

Karickhoff, S. W., Brown, D. S., and Scott, T. A. (1979). "Sorption of hydrophobic pollutants of natural sediments." *Water Res.,* 13, 241–248.

Kennedy, L. G., Everett, J. W., Dewers, T., Pickins, W., and Edwards, D. (1999). "Application of mineral iron and sulfide analysis to evaluate natural attenuation at fuel contaminated site." *J. Environ. Eng.,* 125(1), 47–56.

Korom, S. F., McFarland, M. J., and Sims, R. C. (1996). "Reduced sediments: A factor in the design of subsurface oxidant delivery." *Ground Water Monit. Remediat.,* 16(1), 100–105.

Lendvay, J. M., Sauck, W. A., McCormick, M. L., Barcelona, M. J., Kampbell, D. H., Wilson, J. T., and Adriaens, P. (1998). "Geophysical characterization, redox zonation, and contaminant distribution at a groundwater/surface water interface." *Water Resour. Res.,* 34(12), 3545–3559.

Lovley, D. R., and Phillips, E. J. P. (1986). "Availability of ferric iron for microbial reduction in bottom sediments of the freshwater tidal Potomac river." *Appl. Environ. Microbiol.,* 52(4), 751–757.

Lovley, D. R., and Phillips, E. J. P. (1987). "Rapid assay for microbially reducible ferric iron in aquatic sediments." *Appl. Environ. Microbiol.,* 54(7), 1536–1540.

Lovley, D. R., and Phillips, E. J. P. (1988). "Novel mode of microbial energy metabolism: organic carbon oxidation coupled to dissimilatory reduction of iron or manganese." *Appl. Environ. Microbiol.,* 54(6), 1472–1480.

Lyon, W. G., Glass, R. L., Ye, M. Y., and Vela, N. (1997). "Development of a rapid iron extraction method using 0.5 M HCl 1. Application to samples from George AFB." ManTech Environmental Research Corp., Ada, Okla, 25pp.

Marinelli, F., and Durnford, D. S. (1996). "LNAPL thickness in monitoring wells considering hysteresis and entrapment." *Ground Water,* 34(3), 405–414.

McNab, W. W., and Dooher, B. P. (1998). "A critique of a steady-state analytical method for estimating contaminant degradation rates." *Ground Water,* (36)6, 983–987.

Newell, C., Acree, S., Ross, R., and Huling, S. G. (1995). *Light Nonaqueous Phase Liquids,* EPA Ground Water Issue Paper No. EPA/540/S-95/500.

Pardieck, D. L., Bouwer, E. J., and Stone, A. T. (1992). "Hydrogen peroxide use to increase oxidant capacity for in situ bioremediation of contaminated soils and aquifers: a review." *J. Contam. Hydrol.,* 9(3), 221–242.

Rifai, H. S., Newell, C. J., Gonzales, J. R., Dendrou, S., Dendrou, B., Kennedy, L., and Wilson, J. T. (1998). *Bioplume III Natural Attenuation Decision Support System, User's Manual Version 1.0.* U.S. EPA Robert S. Kerr Environmental Research Center, National Risk Management Research Laboratory, EPA/600/R-98/010.

Roden, E. E., and Zachara, J. M. (1996). "Microbial reduction of crystalline iron(III) oxides: Influence of oxide surface area and potential for cell growth." *Environ. Sci. Technol.,* 30(5), 1618–1628.

Spain, J. C., Milligan, J. D., Downey, D. C., and Slaughter, J. K. (1989). "Excessive bacterial decomposition of H_2O_2 during enhanced biodegradation." *Ground Water,* 27(2), 163–167.

Suflita, J. M., Gibson, S. A., and Beemann, R. E. (1988). "Anaerobic biotransformation of pollutant chemicals in aquifers." *J. Ind. Microbiol.,* 3, 179–194.

U.S. Department of Health and Human Services. (1993). "Agency for Toxic Substances and Disease Registry." Toxicological Profile for Jet Fuels JP-4 and JP-7 (ATSDR-TP-93-17).

U.S. EPA. (1990). Subsurface Contamination Reference Guide. EPA/540/2-90/011.

Vroblesky, D. A., and Chapelle, F. H. (1994). "Temporal and spatial changes of terminal-electron accepting processes in a petroleum hydrocarbon contaminated aquifer and the significance of biodegradation." *Water Resour. Res.,* 30(5), 1561–1570.

Weaver, J. M., Charbeneau, R. J., Taux, J. D., Lien, B. K., and Provost, J. B. (1994). The Hydrocarbon Spill Screening Model (HSSM) Volume 1: User's Guide. U.S. EPA, Robert S. Kerr Environmental Research Laboratory, Ada, OK, EPA/600/R-94/039a.